Beilstein Journal of Organic Chemistry

Synthesis of ethoxy dibenzooxaphosphorin oxides through palladium-catalyzed C(sp^2)–H activation/C–O formation

Seohyun Shin[‡1,2], Dongjin Kang[‡1,2], Woo Hyung Jeon[1,2] and Phil Ho Lee[*1,2]

Full Research Paper

Open Access

Address:
[1]Center for Catalytic Organic Reactions, National Creative Research Laboratory (NCRL), Chuncheon 200-701, Republic of Korea and [2]Department of Chemistry, Kangwon National University, Chuncheon 200-701, Republic of Korea

Email:
Phil Ho Lee[*] - phlee@kangwon.ac.kr

* Corresponding author ‡ Equal contributors

Keywords:
C–H activation; catalysis; cyclization; palladium; phosphorus heterocyclic compound

Beilstein J. Org. Chem. **2014,** *10,* 1220–1227.
doi:10.3762/bjoc.10.120

Received: 08 February 2014
Accepted: 09 April 2014
Published: 23 May 2014

This article is part of the Thematic Series "Organophosphorus chemistry" and is dedicated to Professor Bong Rae Cho (Korea University) on the occasion of his honorable retirement.

Guest Editor: P. R. Hanson

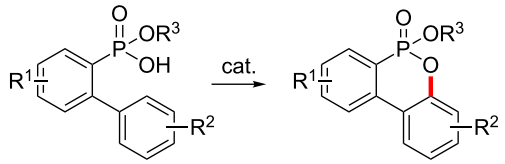
Abstract

We report an efficient Pd-catalyzed C(sp^2)–H activation/C–O bond formation for the synthesis of ethoxy dibenzooxaphosphorin oxides from 2-(aryl)arylphosphonic acid monoethyl esters under aerobic conditions.

Introduction

Unreactive C(sp^2)–H and C(sp^3)–H bonds are ubiquitous in organic compounds [1-7], so that the development of methods for the transition metal-catalyzed C–H activation is one of the challenging goals in organic synthesis. Especially, the development of synthetic methods of C–heteroatom bond formation via C–H activation has received attention owing to the omnipresence of heterocyclic compounds in nature [8]. Recently, it has been demonstrated that the intramolecular bond formation between a heteroatom and a vicinal unreactive C–H is an efficient method for the synthesis of heterocycles [9-17]. Although C–H activation/C–N formation has been widely used for the synthesis of azaheterocycles, the preparation of oxaheterocycles via C–H activation/C–O formation has been described a lot less, because the energy correlation between the HOMO of the Pd–O bond and the LUMO of the Pd–C bond is unfavorable and the Pd–O bond has a significantly ionic character [18-23]. To expand this scope, we are interested in the development of C–H activation/C–O formation by means of new directing groups. Recently, a variety of C–H activations by using new phosphoryl-related directing groups have been reported by our

[24-32] and other groups [33-41]. More recently, we developed a method allowing for synthetic access to benzoxaphosphole 1- and 2-oxides starting from phosphonic and phosphinic acids via Pd-catalyzed C(sp^2 and sp^3)–H activation/C–O formation [42]. In this context, we herein report the synthetic method of alkoxy dibenzooxaphosphorin oxides from 2-(aryl)arylphosphonic acid monoesters via Pd-catalyzed C(sp^2)–H activation/C–O formation (Scheme 1).



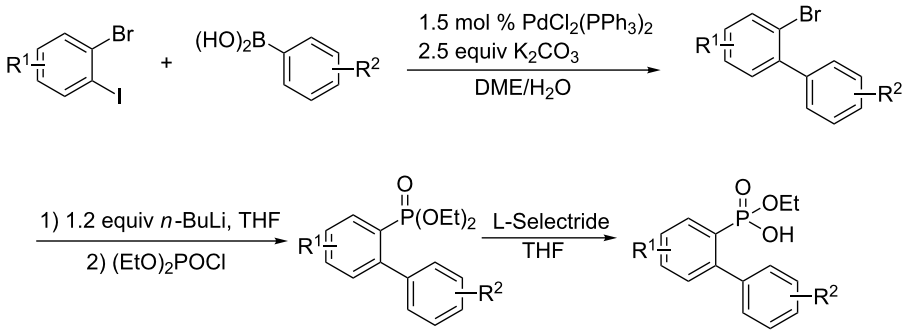
Scheme 1: Synthesis of alkoxy dibenzooxaphosphorin oxides by C(sp^2)–H activation/C–O formation.

Results and Discussion

First, a wide range of 2-(aryl)arylphosphonic acid monoethyl esters were efficiently prepared by a Suzuki reaction of 2-bromoiodoarenes with arylboronic acids, a lithium bromide exchange reaction of 2-bromobiaryls followed by diethylphosphinylation with diethyl chlorophosphate, and the C–O cleavage of diethyl 2-(aryl)arylphosphonates by using L-Selectride (Scheme 2).

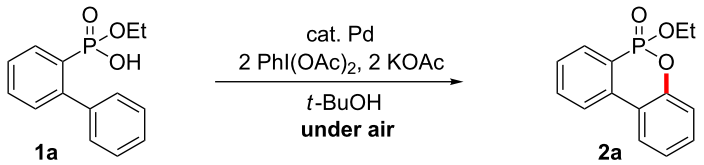
The C–H activation/C–O formation of 2-(phenyl)phenylphosphonic acid monoethyl ester (**1a**) was examined with a variety of oxidants and bases in the presence of $Pd(OAc)_2$. A multitude of oxidants such as $K_2S_2O_8$, BQ, benzoyl peroxide, $PhI(TFA)_2$, $Cu(OAc)_2$, $CuCl_2$, CuBr, AgOAc, Ag_2CO_3 and Ag_2O did not produce the cyclized product **2a** (see Supporting Information File 1). However, $PhI(OAc)_2$, which is an efficient oxidant for the Pd(II)/Pd(IV) catalytic cycle, gave **2a** in 30% yield in *t*-butanol (80 °C for 16 h; Table 1, entry 1) [19,43-47]. In addition, various bases were examined. Although NaOAc, CsOAc, CsF and CsOPiv afforded **2a** in yields ranging from 42% to 52%, KOAc gave the best result (57%) in the presence of $PhI(OAc)_2$ in *tert*-butanol (see Supporting Information File 1). *tert*-Butanol gave the best result among the solvents DCE, dioxane, ACN, *t*-AmOH, DMF, HFIP, THF, toluene, TFA and MeOH (see Supporting Information File 1). With this preliminary result in hand, we investigated a variety of organic acids as ligands in an effort to improve the catalytic efficiency (Scheme 3). However, these attempts provided no improvement (Table 1, entries 2–4). Finally, we discovered that easily accessible monoprotected amino acids, which have recently been established as efficient ligands in C–H activations [48-50], increased the yield (Table 1, entries 5–10). Among the investigated ligands, *N*-acetyl-*L*-leucine (L9) gave the best results (Table 1, entry 10). After examination of the reaction temperature (Table 1, entries 11–13) and time (Table 1, entries 14–16), the oxidative cyclization using $PhI(OAc)_2$ (2 equiv) and KOAc (2 equiv) in the presence of $Pd(OAc)_2$ (10 mol %) and L9 (30 mol %) gave the best result under aerobic conditions, affording **2a** in 61% yield (isolated yield 55%, Table 1, entry 16). Both $Pd(TFA)_2$ and $Pd(OTf)_2{\cdot}H_2O$ gave inferior results compared to $Pd(OAc)_2$ (Table 1, entries 17 and 18).

To ascertain the scope of the Pd-catalyzed C–H activation followed by the C–O formation, a wide range of 2-(aryl)phenylphosphonic acid monoethyl esters **1** were examined under the optimized reaction conditions (Scheme 4). Phenylphosphonic acid monoethyl ester **1b** with a 2-methyl group on the phenyl ring was transformed to the desired dibenzooxaphosphorin oxide **2b** in 53% yield. Phenylphosphonic acid monoethyl esters (**1c**) with a 3-methyl group were selectively converted to the cyclized products (**2c**) in 66% yield due to steric effects. In the case of 4-*tert*-butyl, the desired product



Scheme 2: Preparation of 2-(aryl)arylphosphonic acid monoethyl esters.

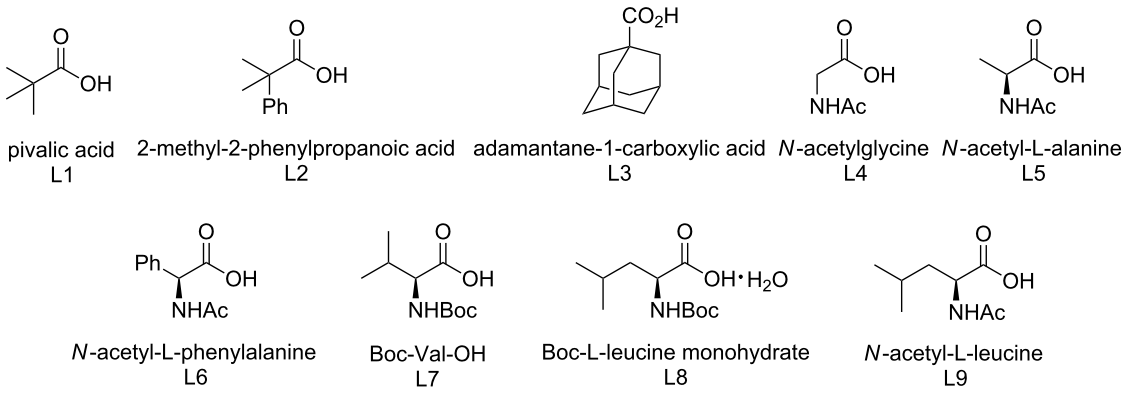
Table 1: Optimization studies for the cyclization of 2-(phenyl)phenylphosphonic acid monoethyl esters.



1a **2a**

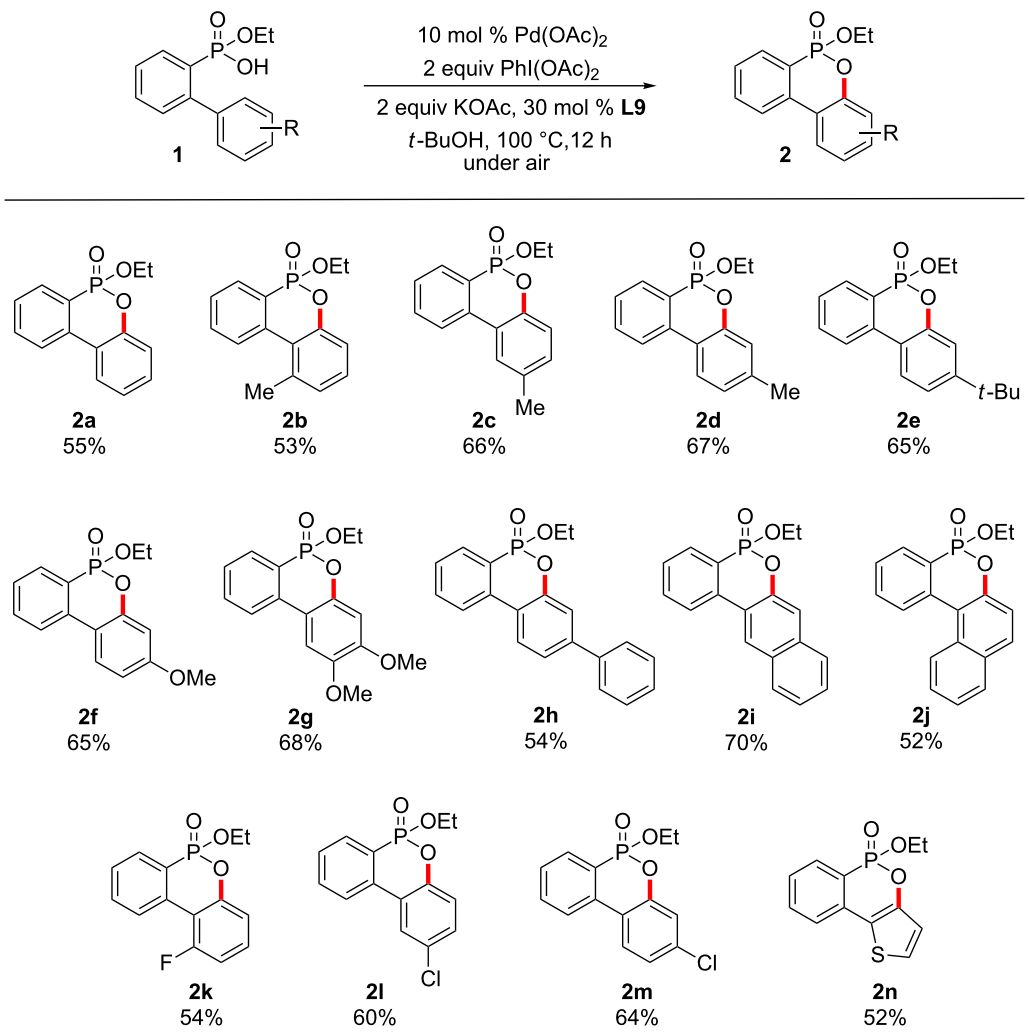
entry	cat. Pd	ligand	*T* [°C]	*t* [h]	yield[a] [%]
1	10 mol % $Pd(OAc)_2$	—	80	16	30
2	10 mol % $Pd(OAc)_2$	30 mol % L1	80	16	23
3	10 mol % $Pd(OAc)_2$	30 mol % L2	80	16	34
4	10 mol % $Pd(OAc)_2$	30 mol % L3	80	16	28
5	10 mol % $Pd(OAc)_2$	30 mol % L4	80	16	48
6	10 mol % $Pd(OAc)_2$	30 mol % L5	80	16	48
7	10 mol % $Pd(OAc)_2$	30 mol % L6	80	16	54
8	10 mol % $Pd(OAc)_2$	30 mol % L7	80	16	53
9	10 mol % $Pd(OAc)_2$	30 mol % L8	80	16	51
10	10 mol % $Pd(OAc)_2$	30 mol % L9	80	16	57
11	10 mol % $Pd(OAc)_2$	30 mol % L9	60	16	20
12	10 mol % $Pd(OAc)_2$	30 mol % L9	100	16	61
13	10 mol % $Pd(OAc)_2$	30 mol % L9	120	16	50
14	10 mol % $Pd(OAc)_2$	30 mol % L9	100	4	45
15	10 mol % $Pd(OAc)_2$	30 mol % L9	100	8	51
16	**10 mol % $Pd(OAc)_2$**	**30 mol % L9**	**100**	**12**	**61(55)**
17	10 mol % $Pd(TFA)_2$	30 mol % L9	100	12	53
18	10 mol % $Pd(OTf)_2{\cdot}H_2O$	30 mol % L9	100	12	45

[a]Yields were determined by ^1H NMR with CH_2Br_2 as an internal standard. The number in parentheses is the isolated yield.



Scheme 3: A variety of organic acids and monoprotected amino acids as ligands.

2e was obtained in 65% yield. Substrate **1f**, characterized by an electron-donating 4-methoxy group, was cyclized to dibenzooxaphosphorin oxide **2f** in 65% yield under aerobic conditions. The present method worked equally well with 3,4-dimethoxyphenyl-substituted phenylphosphonic acid monoethyl ester **1g**. Phenylphosphonic acid monoethyl ester **1h** with a 4-phenyl group on the phenyl ring turned out to be compatible with the reaction conditions. As anticipated, 2-naphthyl-substituted phenylphosphonic acid monoethyl ester **1i** underwent the Pd-catalyzed oxidative cyclization regioselectively at the sterically less hindered position to afford the desired dibenzooxaphosphorin oxide **2i** in 70% yield. We were pleased to

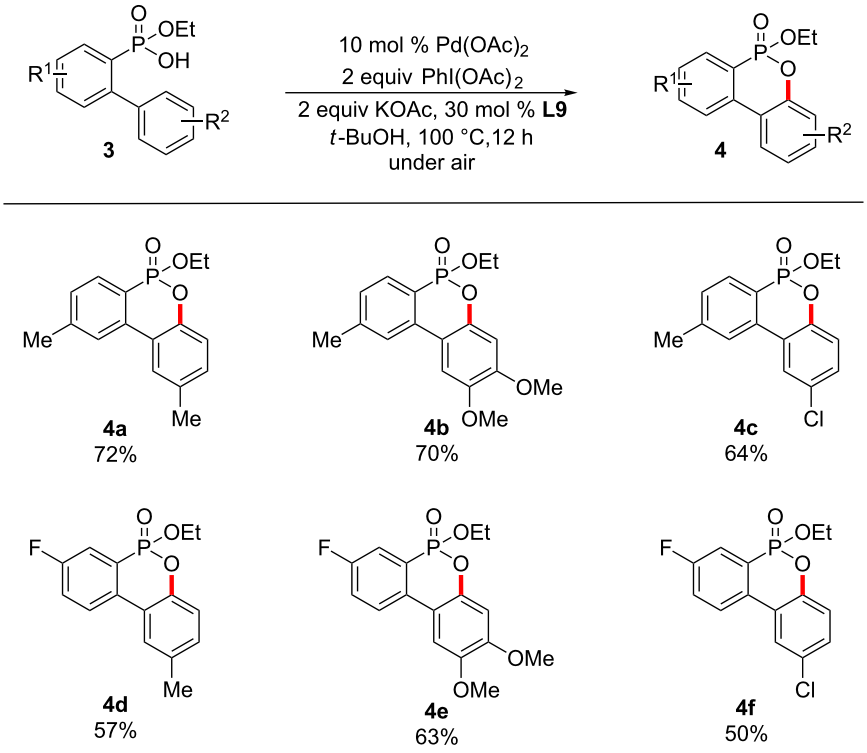


Scheme 4: Cyclization of 2-arylphenylphosphonic acid monoethyl esters.

obtain **2j** by a Pd-catalyzed oxidative cyclization of 1-naphthyl-substituted phenylphosphonic acid monoethyl ester **1j**. 2-(Aryl)phenylphosphonic acid monoethyl esters **1k**, **1l** and **1m** with an electron-withdrawing fluoro or chloro group on the phenyl ring were subjected to the oxidative cyclization to deliver the desired products **2k**, **2l** and **2m** in yields ranging from 54% and 64%. In particular, the tolerance of the chloro groups may be of importance for a subsequent catalytic cross-coupling reaction. Substrate **1n**, which contains a 2-thiophenyl moiety, was subjected to the cyclization affording **2n** in 52% yield. The preparation of 2-arylphenylphosphonic acid monoethyl esters with a nitro, difluoro, or ethoxycarbonyl group failed.

Next, the Pd-catalyzed oxidative cyclization of 2-(aryl)arylphosphonic acid monoethyl esters **3** were examined to demonstrate the efficiency of the present method (Scheme 5). 4-Methylphenylphosphonic acid monoethyl esters **3a** and **3b** with a 3-methyl- and 3,4-dimethoxyphenyl group at 2-position turned out to be compatible with the Pd-catalyzed oxidative cyclization. There are no regioisomers formed due to steric effects. Substrate **3c** bearing a chloro group was selectively cyclized to afford **4c** in 64% yield. To our delight, the present method worked equally well even if a fluoro group on the phenyl ring is present. 3-Fluorophenylphosphonic acid monoethyl esters **3d**, **3e** and **3f** with 3-methyl-, 3,4-dimethoxy and 3-chlorophenyl groups at the 2-position selectively underwent the oxidative cyclization to give the corresponding cyclized products **4d**, **4e** and **4f** in yields ranging from 50% and 63%.

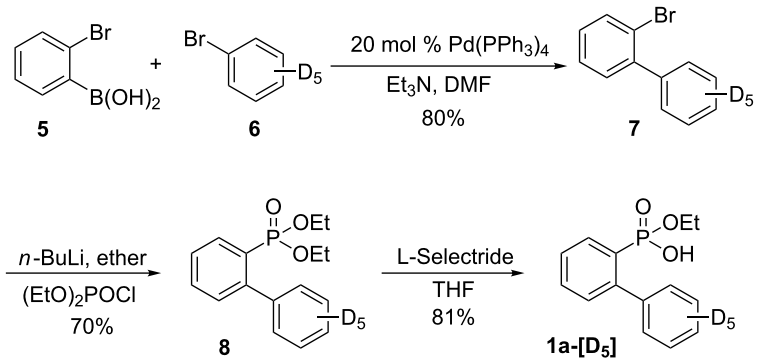
We carried out kinetic isotope effect (KIE) studies to prove the reaction mechanism (see Scheme 8). The required deuterium-labeled 2-(phenyl)phenylphosphonic acid monoethyl ester



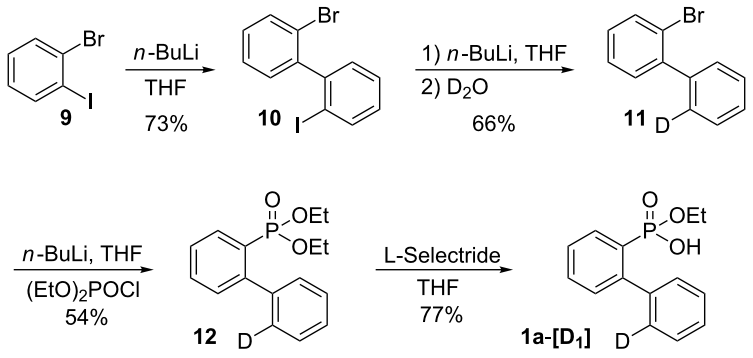
Scheme 5: Cyclization of 2-(aryl)arylphosphonic acid monoethyl esters.

1a-[D_5] was efficiently prepared by a Suzuki reaction of deuterated bromobenzene (**6**) with 2-bromophenylboronic acid (**5**), a lithium bromide exchange reaction of 2-bromo deuterated biphenyl **7** followed by diethylphosphinylation with diethyl chlorophosphate, and C–O cleavage of diethyl 2-(phenyl)-phenylphosphonate by using L-Selectride (Scheme 6). In addition, the deuterium-labeled 2-(phenyl)phenylphosphonic acid monoethyl ester **1a-[D_1]** was obtained by the lithium bromide exchange reaction of 2‘-bromo-2-iodo-1,1‘-biphenyl (**10**) and the treatment of D_2O, diethylphosphinylation with diethyl chlorophosphate, and C–O cleavage of diethyl 2-(phenyl)-phenylphosphonate by using L-Selectride (Scheme 7).

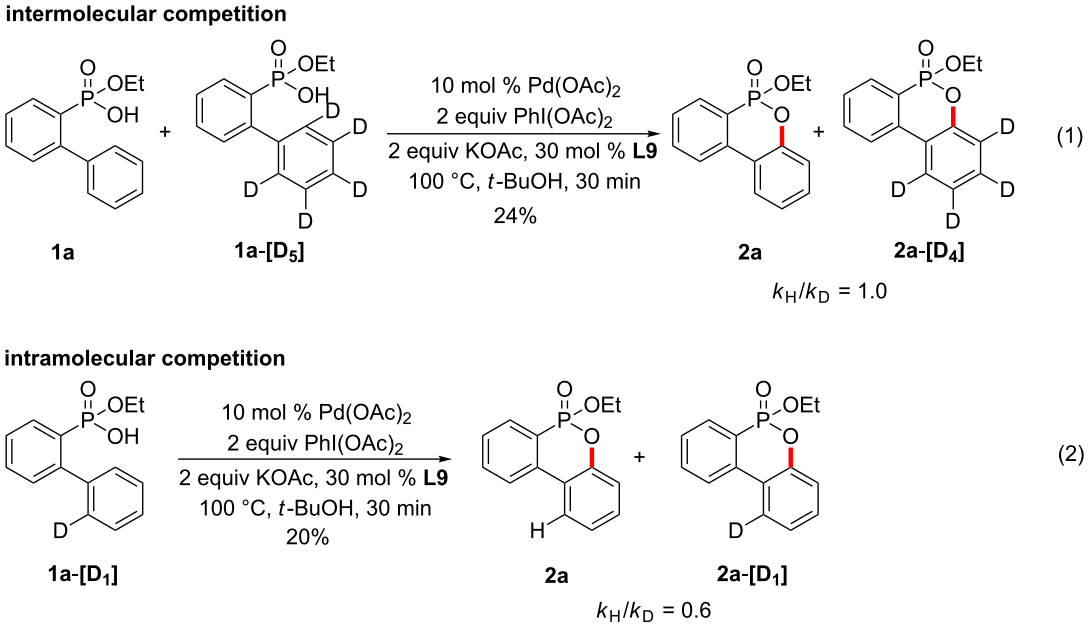
In the case of an intermolecular competition reaction using **1a** and **1a-[D_5]**, a KIE was detected (k_H/k_D = 1.0; Scheme 8, reaction 1) [51,52]. Also, an intramolecular competition reaction



Scheme 6: Preparation of **1a-[D_5]**.



Scheme 7: Preparation of **1a-[D_1]**.



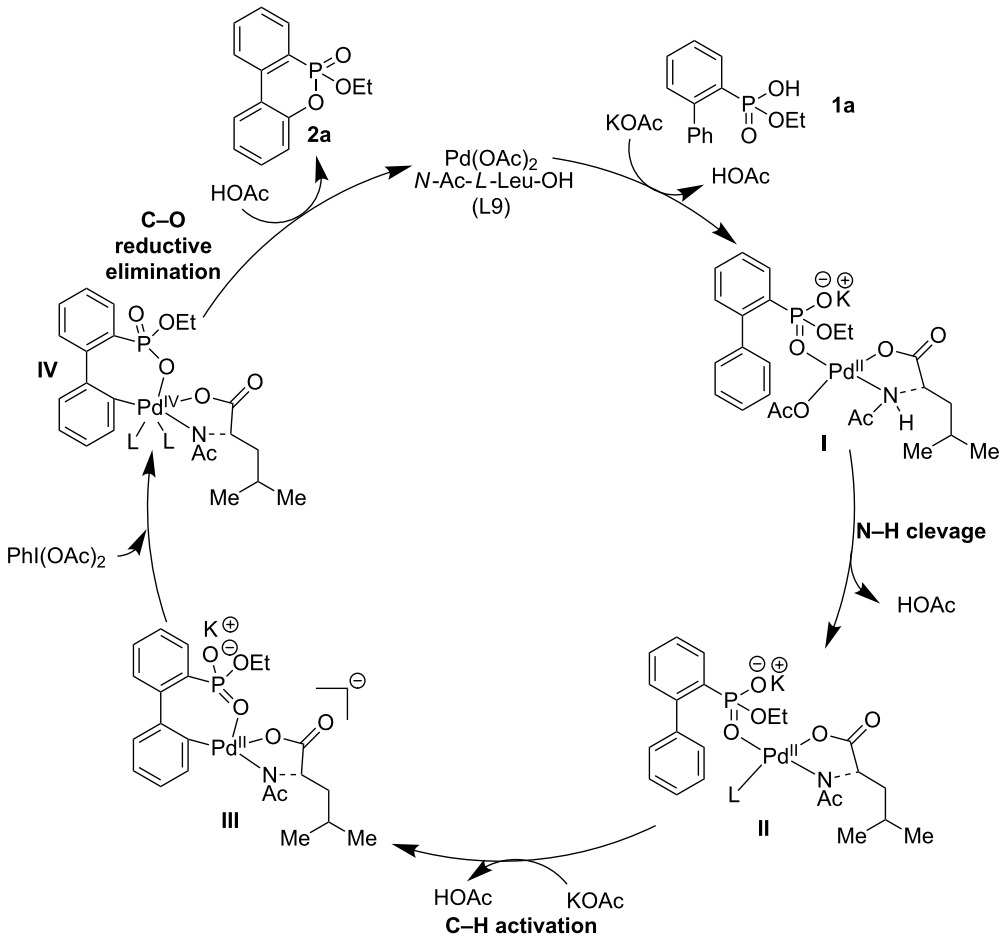
Scheme 8: Studies with isotopically labelled compounds.

using **1a-[D_1]** was carried out to give KIE (k_H/k_D = 0.6; Scheme 8, reaction 2). These results indicate that the C–H cleavage at the *ortho*-position of 2-(phenyl)phenylphosphonic acid monoethyl ester is not involved in the rate-limiting step and the C–H bond metallation is reversible.

To elucidate the mechanism of the present reaction, the reaction was conducted with a stoichiometric amount of $Pd(OAc)_2$ and without the oxidant $PhI(OAc)_2$. However, no cyclized product was observed. This result indicates that the C–O reductive elimination from Pd(II) is not favorable. Because both the intermolecular and intramolecular competition experiments exhibited no significant kinetic isotope effect (k_H/k_D = 1.0 and 0.6; Scheme 8), we hypothesize that the C–O reductive elimination step is the rate-determining step. A feasible mechanism involving the Pd(II)/Pd(IV) catalytic cycle is described in Scheme 9. The C–H activation might be efficiently accelerated by the N–H activation propelled by *N*-Ac-*L*-Leu-OH (L9) as a ligand [53-55], resulting in the formation of palladacycle **III**. Thereafter, ethoxy dibenzooxaphosphorin oxide **2a** is obtained from the oxidation of the Pd(II) to Pd(IV) species **IV** and the subsequent C–O reductive elimination.

Conclusion

In this paper, we have developed an efficient synthetic method for a wide range of ethoxy dibenzooxaphosphorin oxides



Scheme 9: A plausible mechanism.

starting from 2-(aryl)arylphosphonic acid monoethyl esters and employing Pd-catalyzed C(sp^2)–H activation/C–O formation under aerobic conditions. Oxidative cyclization by means of a Pd(II)/Pd(IV) catalytic cycle might play a role in the mechanism of the present reaction.

Supporting Information

Supporting Information File 1

Experimental procedures, characterization data, and ^{1}H and ^{13}C NMR spectra of new compounds.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-10-120-S1.pdf]

Acknowledgements

This work was supported by a grant from the National Research Foundation of Korea (NRF) funded by the Korea government (MSIP) (2014001403). This study was also supported by a 2013 Research Grant from Kangwon National University (No. 120131246).

References

1. Murai, S.; Alper, H.; Gossage, R. A.; Grushin, V. V.; Hidai, M.; Ito, Y.; Jones, W. D.; Kakiuchi, F.; van Koten, G.; Lin, Y.-S.; Mizobe, Y.; Murai, S.; Murakami, M.; Richmond, T. G.; Sen, A.; Suginome, M.; Yamamoto, A., Eds. *Activation of Unreactive Bonds and Organic Synthesis;* Springer: Berlin, 1999. doi:10.1007/3-540-68525-1
2. Dyker, G., Ed. *Handbook of C–H Transformations;* Wiley-VCH: Weinheim, 2005. doi:10.1002/9783527619450
3. Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010,** *110,* 1147. doi:10.1021/cr900184e
4. Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010,** *110,* 624. doi:10.1021/cr900005n
5. Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011,** *111,* 1293. doi:10.1021/cr100198w
6. Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011,** *40,* 5068. doi:10.1039/c1cs15082k
7. Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011,** *111,* 1215. doi:10.1021/cr100280d
8. Li, J.-J.; Corey, E. J., Eds. *Name Reactions in Heterocyclic Chemistry;* Wiley-Interscience: Hoboken, NJ, 2005. doi:10.1002/0471704156
9. Thansandote, P.; Lautens, M. *Chem.–Eur. J.* **2009,** *15,* 5874. doi:10.1002/chem.200900281
10. Espino, C. G.; Wehn, P. M.; Chow, J.; Du Bois, J. *J. Am. Chem. Soc.* **2001,** *123,* 6935. doi:10.1021/ja011033x

11. Liang, J.-L.; Yuan, S.-X.; Huang, J.-S.; Che, C.-M. *J. Org. Chem.* **2004,** *69,* 3610. doi:10.1021/jo0358877
12. Jordan-Hore, J. A.; Johansson, C. C. C.; Gulias, M.; Beck, E. M.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008,** *130,* 16184. doi:10.1021/ja806543s
13. Mei, T.-S.; Wang, X.; Yu, J.-Q. *J. Am. Chem. Soc.* **2009,** *131,* 10806. doi:10.1021/ja904709b
14. Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2008,** *130,* 14058. doi:10.1021/ja807129e
15. Neumann, J. J.; Rakshit, S.; Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2009,** *48,* 6892. doi:10.1002/anie.200903035
16. Inamoto, K.; Saito, T.; Katsuno, M.; Sakamoto, T.; Hiroya, K. *Org. Lett.* **2007,** *9,* 2931. doi:10.1021/ol0711117
17. Wang, H.; Wang, Y.; Peng, C.; Zhang, J.; Zhu, Q. *J. Am. Chem. Soc.* **2010,** *132,* 13217. doi:10.1021/ja1067993
18. Hartwig, J. F. *Inorg. Chem.* **2007,** *46,* 1936. doi:10.1021/ic061926w
19. Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004,** *126,* 2300. doi:10.1021/ja031543m
20. Novák, P.; Correa, A.; Gallardo-Donaire, J.; Martin, R. *Angew. Chem., Int. Ed.* **2011,** *50,* 12236. doi:10.1002/anie.201105894
21. Gallardo-Donaire, J.; Martin, R. *J. Am. Chem. Soc.* **2013,** *135,* 9350. doi:10.1021/ja4047894
22. Cheng, X.-F.; Li, Y.; Su, Y.-M.; Yin, F.; Wang, J.-Y.; Sheng, J.; Vora, H. U.; Wang, X.-S.; Yu, J.-Q. *J. Am. Chem. Soc.* **2013,** *135,* 1236. doi:10.1021/ja311259x
23. Yang, M.; Jiang, X.; Shi, W.-J.; Zhu, Q.-L.; Shi, Z.-J. *Org. Lett.* **2013,** *15,* 690. doi:10.1021/ol303569b
24. Seo, J.; Park, Y.; Jeon, I.; Ryu, T.; Park, S.; Lee, P. H. *Org. Lett.* **2013,** *15,* 3358. doi:10.1021/ol401407v
25. Chary, B. C.; Kim, S.; Park, Y.; Kim, J.; Lee, P. H. *Org. Lett.* **2013,** *15,* 2692. doi:10.1021/ol4009987
26. Chan, L. Y.; Kim, S.; Ryu, T.; Lee, P. H. *Chem. Commun.* **2013,** *49,* 4682. doi:10.1039/c3cc41107a
27. Ryu, T.; Kim, J.; Park, Y.; Kim, S.; Lee, P. H. *Org. Lett.* **2013,** *15,* 3986. doi:10.1021/ol401775t
28. Park, S.; Seo, B.; Shin, S.; Son, J.-Y.; Lee, P. H. *Chem. Commun.* **2013,** *49,* 8671. doi:10.1039/c3cc44995e
29. Mo, J.; Lim, S.; Park, S.; Ryu, T.; Kim, S.; Lee, P. H. *RSC Adv.* **2013,** *3,* 18296. doi:10.1039/c3ra43764g
30. Park, Y.; Seo, J.; Park, S.; Yoo, E. J.; Lee, P. H. *Chem.–Eur. J.* **2013,** *19,* 16461. doi:10.1002/chem.201302652
31. Park, Y.; Jeon, I.; Shin, S.; Min, J.; Lee, P. H. *J. Org. Chem.* **2013,** *78,* 10209. doi:10.1021/jo401608v
32. Kang, D.; Cho, J.; Lee, P. H. *Chem. Commun.* **2013,** *49,* 10501. doi:10.1039/c3cc45874a
33. Meng, X.; Kim, S. *Org. Lett.* **2013,** *15,* 1910. doi:10.1021/ol400565r
34. Chan, L. Y.; Cheong, L.; Kim, S. *Org. Lett.* **2013,** *15,* 2186. doi:10.1021/ol400732q
35. Jeon, W. H.; Lee, T. S.; Kim, E. J.; Moon, B.; Kang, J. *Tetrahedron* **2013,** *69,* 5152. doi:10.1016/j.tet.2013.04.067
36. Hu, R.-B.; Zhang, H.; Zhang, X.-Y.; Yang, S.-D. *Chem. Commun.* **2014,** *50,* 2193. doi:10.1039/c3cc49050e
37. Wang, H.-L.; Hu, R.-B.; Zhang, H.; Zou, A.-X.; Yang, S.-D. *Org. Lett.* **2013,** *15,* 5302. doi:10.1021/ol402577p
38. Zhang, H.-Y.; Yi, H.-M.; Wang, G.-W.; Yang, B.; Yang, S.-D. *Org. Lett.* **2013,** *15,* 6186. doi:10.1021/ol403028a
39. Unoh, Y.; Hashimoto, Y.; Takeda, D.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2013,** *15,* 3258. doi:10.1021/ol4012794
40. Itoh, M.; Hashimoto, Y.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2013,** *78,* 8098. doi:10.1021/jo401393b
41. Zhao, D.; Nimphius, C.; Lindale, M.; Glorius, F. *Org. Lett.* **2013,** *15,* 4504. doi:10.1021/ol402053n
42. Eom, D.; Jeong, Y.; Kim, Y. R.; Lee, E.; Choi, W.; Lee, P. H. *Org. Lett.* **2013,** *15,* 5210. doi:10.1021/ol402736v
43. Yoneyama, T.; Crabtree, R. H. *J. Mol. Catal. A: Chem.* **1996,** *108,* 35. doi:10.1016/1381-1169(95)00289-8
44. Muñiz, K. *Angew. Chem., Int. Ed.* **2009,** *48,* 9412. doi:10.1002/anie.200903671
45. Wei, Y.; Yoshikai, N. *Org. Lett.* **2011,** *13,* 5504. doi:10.1021/ol202229w
46. Zhang, S.-Y.; He, G.; Zhao, Y.; Wright, K.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2012,** *134,* 7313. doi:10.1021/ja3023972
47. Hickman, A. J.; Sanford, M. S. *Nature* **2012,** *484,* 177. doi:10.1038/nature11008
48. Wang, D.-H.; Engle, K. M.; Shi, B.-F.; Yu, J.-Q. *Science* **2010,** *327,* 315. doi:10.1126/science.1182512
49. Lu, Y.; Wang, D.-H.; Engle, K. M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010,** *132,* 5916. doi:10.1021/ja101909t
50. Cheng, G.-J.; Yang, Y.-F.; Liu, P.; Chen, P.; Sun, T.-Y.; Li, G.; Zhang, X.; Houk, K. N.; Yu, J.-Q.; Wu, W.-D. *J. Am. Chem. Soc.* **2014,** *136,* 894. doi:10.1021/ja411683n
51. Jones, W. D. *Acc. Chem. Res.* **2003,** *36,* 140. doi:10.1021/ar020148i
52. Kakiuchi, F.; Matsuura, Y.; Kan, S.; Chatani, N. *J. Am. Chem. Soc.* **2005,** *127,* 5936. doi:10.1021/ja043334n
53. Musaev, D. G.; Kaledin, A. L.; Shi, B.-F.; Yu, J.-Q. *J. Am. Chem. Soc.* **2012,** *134,* 1690. doi:10.1021/ja208661v
54. Baxter, R. D.; Sale, D.; Engle, K. M.; Yu, J.-Q.; Blackmond, D. G. *J. Am. Chem. Soc.* **2012,** *134,* 4600. doi:10.1021/ja207634t
55. Li, Y.; Ding, Y.-J.; Wang, J.-Y.; Su, Y.-M.; Wang, X.-S. *Org. Lett.* **2013,** *15,* 2574. doi:10.1021/ol400877q

License and Terms